



# A multi-year observation of nitrous oxide at the Boknis Eck Time Series Station in the Eckernförde Bay (southwestern Baltic Sea)

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**Abstract.** Nitrous oxide (N<sub>2</sub>O) is a potent greenhouse gas, and it is involved in stratospheric ozone depletion. Its oceanic production is mainly influenced by dissolved nutrient and oxygen (O<sub>2</sub>) concentrations in the water column. Here we examined the seasonal and annual variations in dissolved N<sub>2</sub>O at the Boknis Eck (BE) Time Series Station located in Eckernförde Bay (southwestern Baltic Sea). Monthly measurements of N<sub>2</sub>O started in July 2005. We found a pronounced seasonal pattern for N<sub>2</sub>O with high concentrations (supersaturations) in winter and early spring and low concentrations (undersaturations) in autumn when hypoxic or anoxic conditions prevail. Unusually low N<sub>2</sub>O concentrations were observed during October 2016–April 2017, which was presumably a result of prolonged anoxia and the subsequent nutrient deficiency. Unusually high N<sub>2</sub>O concentrations were found in November 2017 and this event was linked to the occurrence of upwelling which interrupted N<sub>2</sub>O consumption via denitrification and potentially promoted ammonium oxidation (nitrification) at the oxic–anoxic interface. Nutrient concentrations (such as nitrate, nitrite and phosphate) at BE have been decreasing since the 1980s, but oxygen concentrations in the water column are still decreasing. Our results indicate a close coupling of N<sub>2</sub>O anomalies to O<sub>2</sub> concentration, nutrients, and stratification. Given the long-term trends of declining nutrient and oxygen concentrations at BE, a decrease in N<sub>2</sub>O concentration, and thus emissions, seems likely due to an increasing number of events with low N<sub>2</sub>O concentrations.

## 1 Introduction

Long-term observation with regular measurement intervals can be an effective way to monitor seasonal and inter-annual variabilities as well as to decipher short- and long-term trends of an ecosystem, which are required to make projections of the future ecosystem development (e.g. see Ducklow et al., 2009). Recently, multi-year time series measurements of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas and a major threat to ozone depletion (IPCC, 2013; Ravishankara et al., 2009), have been reported from the coastal upwelling areas off central Chile (Farías et al., 2015), off Goa (Naqvi et al., 2010), in the North Pacific Subtropical Gyre (Wilson et al., 2017), and in Saanich Inlet (Capelle et al., 2018).

N<sub>2</sub>O production in the ocean is generally dominated by microbial nitrification (NH<sub>4</sub><sup>+</sup> → NO<sub>2</sub><sup>−</sup> → NO<sub>3</sub><sup>−</sup>) and denitrification (NO<sub>3</sub><sup>−</sup> → NO<sub>2</sub><sup>−</sup> → N<sub>2</sub>O → N<sub>2</sub>). During bacterial or archaeal nitrification, N<sub>2</sub>O is produced as a by-product with enhanced N<sub>2</sub>O production under low-oxygen (O<sub>2</sub>) conditions (e.g. Goreau et al., 1980; Löscher et al., 2012). N<sub>2</sub>O is produced as an intermediate during bacterial denitrification (Codispoti et al., 2005). N<sub>2</sub>O could be further consumed via denitrification to dinitrogen; however, this process is inhibited with the presence of O<sub>2</sub> because of the low O<sub>2</sub> tolerance of the enzyme involved (Bonin et al., 1989). This incomplete pathway is called partial denitrification and can lead to N<sub>2</sub>O accumulation (e.g. Naqvi et al., 2000; Farías et al., 2009).

The oceans including coastal areas contribute ~ 25 % of the natural and anthropogenic N<sub>2</sub>O emissions (IPCC, 2013), with disproportionately high emissions from coastal and estuarine areas (Bange, 2006). N<sub>2</sub>O emissions from coastal

areas strongly depend on nitrogen inputs (Seitzinger and Kroeze, 1998; Zhang et al., 2010). The increasing input of nitrogen (i.e. eutrophication) has become a worldwide problem in coastal waters leading to enhanced productivity and severe O<sub>2</sub> depletion caused by enhanced degradation of organic matter (Breitburg et al., 2018; Rabalais et al., 2014). The decline in O<sub>2</sub> concentration (i.e. deoxygenation), either in coastal waters or the open ocean, might result in favourable conditions for N<sub>2</sub>O production (Codispoti et al., 2001; Nevins et al., 2003). The results of a model study by Kroeze and Seitzinger (1998) indicated a significant increase in N<sub>2</sub>O in European coastal waters for 2050. Moreover, it has been suggested that N<sub>2</sub>O production and emissions are very likely to increase in the near future, especially in the shallow sub-oxic or anoxic coastal systems (Naqvi et al., 2000; Bange, 2006). However, model projections show a net decrease in future global oceanic N<sub>2</sub>O emission during the 21st century (Martinez-Rey et al., 2015; Landolfi et al., 2017; Battaglia and Joos, 2018).

The Baltic Sea is a nearly enclosed, marginal sea with a very limited access to the open ocean via the North Sea. The restricted water exchange with the North Sea and extensive human activities, such as agriculture, industrial production, and sewage discharge in the catchment area led to high inputs of nutrients to the Baltic Sea. As a result, the areas affected by anoxia have been expanding in the deep basins of the central Baltic Sea (Carstensen et al., 2014). In order to control this situation, the Helsinki Commission (HELCOM) was established in 1974 and a series of measures have been taken to prevent anthropogenic nutrient input into the Baltic Sea. Consequently, the nutrient inputs (by riverine loads, direct point sources, and, for nitrogen, atmospheric deposition) to the Baltic Sea are declining (HELCOM, 2018a). However, the number of low-O<sub>2</sub> (i.e. hypoxic or anoxic) events in coastal waters of the Baltic Sea is increasing and deoxygenation is still going on (Conley et al., 2011; Lennartz et al., 2014). The deoxygenation in the Baltic Sea can affect the production and consumption of N<sub>2</sub>O. Our group has been monitoring dissolved N<sub>2</sub>O concentrations at the Boknis Eck Time Series Station, located in Eckernförde Bay (southwestern Baltic Sea), for more than a decade. In this study, we present monthly measurements of N<sub>2</sub>O and biogeochemical parameters such as nutrients and O<sub>2</sub> from July 2005 to December 2017. The major objectives of our study were: (1) to decipher the seasonal pattern of N<sub>2</sub>O distribution in the water column, (2) to identify short-term and long-term trends of the N<sub>2</sub>O concentrations, (3) to explore the potential role of nutrients and O<sub>2</sub> for N<sub>2</sub>O production and consumption, and (4) to quantify the sea-to-air N<sub>2</sub>O flux density at the time series station.

## 2 Material and methods

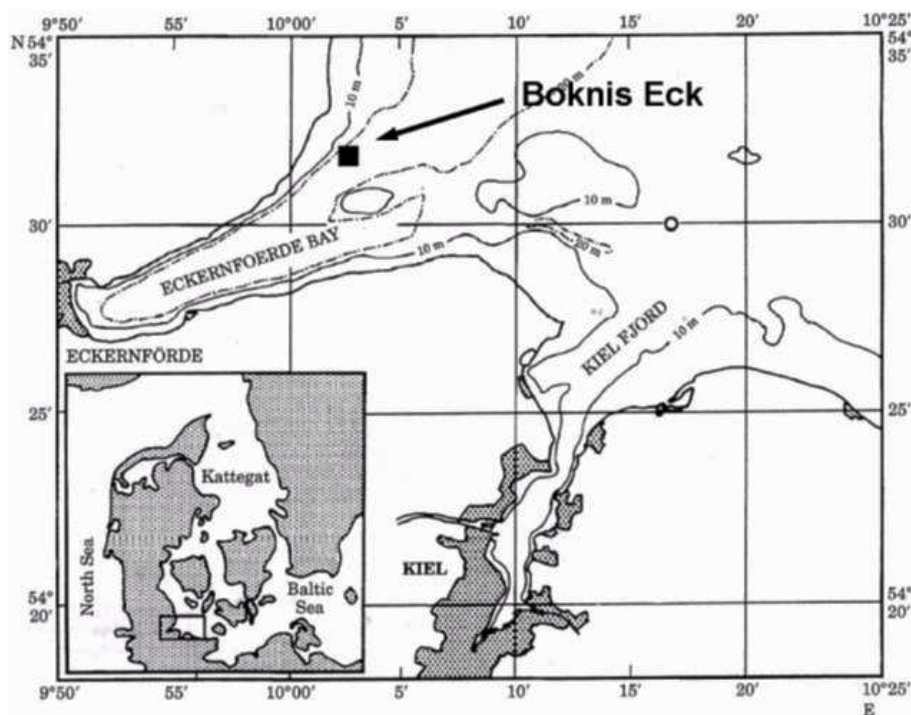
### 2.1 Study site

Sampling at the Boknis Eck (BE) Time Series Station (<https://www.bokniseck.de>) started on 30 April 1957 and, therefore, it is one of the oldest continuously operated time series stations in the world. The BE station is located at the entrance of Eckernförde Bay (54°31' N, 10°02' E; Fig. 1) in the southwestern Baltic Sea. The water depth of the sampling site is 28 m. Various physical, chemical, and biological parameters are measured on a monthly basis (Lennartz et al., 2014). There is no significant river runoff to Eckernförde Bay. Hence, the hydrographical conditions are mainly dominated by saline water input from the North Sea and less saline water from the Baltic Proper, which is typical for that region. Seasonal stratification usually starts to develop in April and lasts until October, during which hypoxia or even anoxia (characterized by the presence of hydrogen sulfide, H<sub>2</sub>S) sporadically occurs, as a result of restricted vertical water exchange and bacterial decomposition of organic matter in the bottom water (Hansen et al., 1999; Lennartz et al., 2014). Thus, BE is a natural laboratory to study the influence of O<sub>2</sub> variations and anthropogenic nutrient loads on N<sub>2</sub>O production and consumption.

### 2.2 Sample collection and measurement

Monthly sampling of N<sub>2</sub>O at the BE Time Series Station started in July 2005. Triplicate samples were collected from six depths (1, 5, 10, 15, 20, and 25 m). Seawater was drawn from 5 L Niskin bottles into 20 mL brown glass vials after overflow. The vials were sealed with rubber stoppers and aluminium caps. The bubble-free samples were poisoned with 50 µL of a saturated mercury chloride (HgCl<sub>2</sub>) solution and then stored in a cool, dark place until measurement. The general storage time before measurements of the N<sub>2</sub>O concentrations was less than 3 months.

The static headspace equilibrium method was adopted to measure the dissolved N<sub>2</sub>O concentrations in the vials. A 10 mL helium (99.9999 %, AirLiquide, Düsseldorf, Germany) headspace was created in each vial with a gas-tight glass syringe (VICI Precision Sampling, Baton Rouge, LA, USA). Samples were vibrated with a vortex (G-560E, Scientific Industries Inc., NY, USA) for 20 s and then left for at least 2 h until equilibrium. A 9.5 mL subsample of the headspace was subsequently injected into a GC-ECD (gas chromatograph equipped with an electron capture detector) system (Hewlett-Packard 5890 Series II, Agilent Technologies, Santa Clara, CA, USA), which was calibrated with two standard gas mixtures (N<sub>2</sub>O in synthetic air, 320 and 1000 ppb, Deuste Steininger GmbH, Mühlhausen, Germany and Westfalen AG, Münster, Germany) prior to the measurement. The average precision of the measurements, calculated as the median standard deviation from triplicate measure-



**Figure 1.** Location of the Boknis Eck Time Series Station in the Eckernförde Bay, southwestern Baltic Sea. (Map from Hansen et al., 1999.)

ments, was 0.4 nM. Triplicates with a standard deviation of  $> 10\%$  were omitted. More details about the  $\text{N}_2\text{O}$  measurement can be found in Kock et al. (2016). Dissolved oxygen ( $\text{O}_2$ ) concentrations were measured by Winkler titrations (Grasshoff et al., 1999). Nutrient concentrations were measured by segmented continuous-flow analysis (SCFA; Grasshoff et al., 1999). A more detailed summary of the parameters measured and methods applied can be found in Lennartz et al. (2014).

### 2.3 Times series analysis

A time series can be decomposed into three main components, i.e. trend, cycle, and residual component (Schlittgen and Streitberg, 2001). We used the Mann–Kendall test and wavelet analysis to detect the trend and periodical cycles in the time series data, respectively. As for the residual component, we highlight unusual high or low  $\text{N}_2\text{O}$  concentrations during 2005–2017 and discuss the potential causes for these events.

#### 2.3.1 Wavelet analysis

In order to decipher periodical cycles of the parameters collected at the BE Time Series Station, a wavelet analysis method was adopted. Wavelet analysis enables the detection of the period and the temporal occurrence of repeated cycles in time series data. One of the requirements for wavelet analysis is a regular, continuous time series. Since there are

data missing (maximum 2 months in a row) in the BE time series, due to terrible weather or the ship's unavailability, missing data were interpolated from the previous and following months. Sampling time varied for every month (usually 20–40 d interval) but for the statistical analysis data were assumed to be regularly spaced as the uncertainty introduced was not significant ( $< 5\%$ ). Considering the band width in both frequency and time domain, a Morlet mother wavelet with a wave number of 6 was chosen (Torrence and Compo, 1998). The mother wavelet was then scaled between the frequency of a half-year cycle and the length of the time series with a step size of 0.25. The wavelet analysis was conducted with the MATLAB code by Torrence and Compo (2004). More information about the method can be found on the website <http://paos.colorado.edu/research/wavelets/> (last access: 23 October 2019).

#### 2.3.2 Mann–Kendall test

Mann–Kendall test (MKT) is a non-parametric statistical test to assess the significance of monotonic trends for time series measurements. It tests the null hypothesis that all variables are randomly distributed against the alternative hypothesis that a monotonic trend, either increase or decrease, exists in the time series on a given significance level  $\alpha$  (here  $\alpha = 0.05$ ). MKT is flexible for data with missing values and the results are not impacted by the magnitude of extreme values, which makes it a widely used test in hydrology and climatology (e.g. Xu et al., 2003; Yang et al., 2004). How-

ever, MKT is sensitive to serial correlation in the time series. The presence of positive serial correlation would increase the probability of trend detection even though no such trend exists (Kulkarni and von Storch, 1995). In order to avoid this situation, data from 12 months were tested individually. It is assumed that there is no residual effect left from the same month last year, considering that the nitrogen species are rapidly biologically cycled. The MATLAB function from Simone (2009) was used for the MKT.

## 2.4 Calculation of saturation and sea-to-air flux density

$\text{N}_2\text{O}$  saturations ( $S_{\text{N}_2\text{O}}$ , %) were calculated as

$$S_{\text{N}_2\text{O}} = 100 \times \text{N}_2\text{O}_{\text{obs}} / \text{N}_2\text{O}_{\text{eq}}, \quad (1)$$

where  $\text{N}_2\text{O}_{\text{obs}}$  and  $\text{N}_2\text{O}_{\text{eq}}$  (nM) are the observed and equilibrated  $\text{N}_2\text{O}$  concentrations in seawater, respectively.  $\text{N}_2\text{O}_{\text{eq}}$  was computed as a function of surface seawater temperature, in situ salinity (Weiss and Price, 1980), and the dry mole fractions of atmospheric  $\text{N}_2\text{O}$  at the time of the sampling. Since the atmospheric  $\text{N}_2\text{O}$  mole fractions were not measured at the BE Time Series Station, atmospheric dry mole fractions of  $\text{N}_2\text{O}$  were derived from the monthly average of  $\text{N}_2\text{O}$  data at Mace Head, Ireland, instead (AGAGE, Advanced Global Atmospheric Gases Experiment, <http://agage.mit.edu/>, last access: 23 October 2019).

$\text{N}_2\text{O}$  flux density ( $F_{\text{N}_2\text{O}}$ ,  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ) was calculated as

$$F_{\text{N}_2\text{O}} = k_{\text{N}_2\text{O}} \times (\text{N}_2\text{O}_{\text{obs}} - \text{N}_2\text{O}_{\text{eq}}), \quad (2)$$

where  $k_{\text{N}_2\text{O}}$  ( $\text{cm h}^{-1}$ ) is the gas transfer velocity calculated with the method given by Nightingale et al. (2000), as a function of the wind speed and the Schmidt number ( $Sc$ ). The wind speed data were obtained from Kiel lighthouse (see <https://www.geomar.de/service/wetter/>, last access: 23 October 2019), which is approximately 20 km away from the BE Time Series Station. The wind speed was normalized to 10 m ( $u_{10}$ ) to calculate  $k_{\text{N}_2\text{O}}$  (Hsu et al., 1994).  $k_{\text{N}_2\text{O}}$  was adjusted by multiplying with  $(Sc/600)^{-0.5}$ , and  $Sc$  was computed as

$$Sc = \nu / D_{\text{N}_2\text{O}}, \quad (3)$$

$$D_{\text{N}_2\text{O}} = 3.16 \times 10^{-6} e^{-18370/RT}, \quad (4)$$

where  $\nu$  is the kinematic viscosity of seawater, which is calculated from the empirical equations given in Siedler and Peters (1986), and  $D_{\text{N}_2\text{O}}$  is the diffusion coefficient of  $\text{N}_2\text{O}$  in seawater.  $R$  is the universal gas constant and  $T$  is the water temperature in kelvin.

## 3 Result and discussion

### 3.1 Overview

$\text{N}_2\text{O}$  concentrations at the BE Time Series Station showed significant temporal and depth-dependent variations from

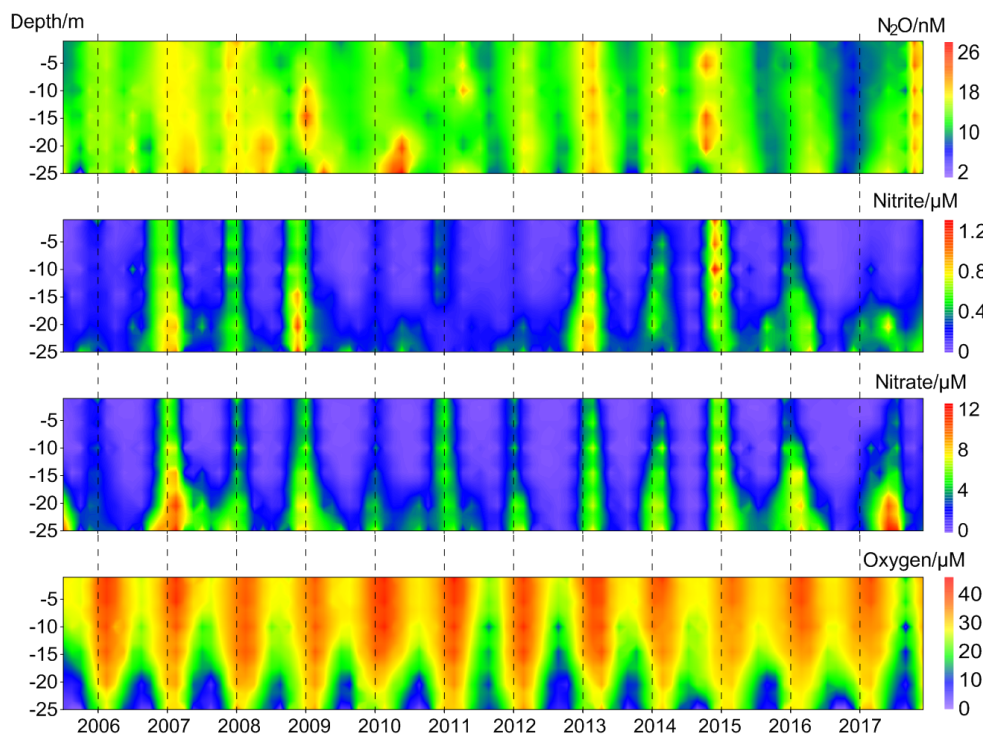
2005 to 2017 (Fig. 2).  $\text{N}_2\text{O}$  concentrations fluctuated between 1.2 and 37.8 nM, with an overall average of  $13.9 \pm 4.2$  nM. This value was higher than the results from the surface water of Station ALOHA ( $5.9\text{--}7.4$  nmol  $\text{kg}^{-1}$ , average  $6.5 \pm 0.3$  nmol  $\text{kg}^{-1}$ ; Wilson et al., 2017), which is reasonable considering the weak anthropogenic impact in the North Pacific Subtropical Gyre. The  $\text{N}_2\text{O}$  concentrations at BE were much lower than those measured at the time series station in the coastal upwelling area off Chile ( $2.9\text{--}492$  nM, average  $39.4 \pm 29.2$  nM in the oxyclines and  $37.6 \pm 23.3$  nM in the bottom waters; Fariás et al., 2015) and a quasi-time-series station off Goa (Naqvi et al., 2010), where significant  $\text{N}_2\text{O}$  accumulations are observed in subsurface waters at both locations. Our measurements were comparable to the time series station from Saanich Inlet ( $\sim 0.5\text{--}37.4$  nM, average 14.7 nM; Capelle et al., 2018), a seasonally anoxic fjord which has similar hydrographic conditions as BE.

$\text{NO}_2^-$  concentrations fluctuated between below the detection limit of 0.1 and 1.6  $\mu\text{M}$ , with an average of  $0.2 \pm 0.3$   $\mu\text{M}$ .  $\text{NO}_3^-$  concentrations varied from below the detection limit of 0.3 to 17.9  $\mu\text{M}$ , with an average of  $2.0 \pm 2.8$   $\mu\text{M}$ . The temporal and spatial distributions of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) were similar during 2005–2017. A clear  $\text{O}_2$  seasonality can be seen with severe  $\text{O}_2$  depletion in the bottom waters during summer and autumn. Anoxia with the presence of  $\text{H}_2\text{S}$  were detected in September and October 2005, September 2007, September and October 2014, and September–November 2016. All of the extremely low  $\text{N}_2\text{O}$  concentrations ( $< 5$  nM) were observed in the bottom waters in autumn, coinciding with hypoxia or anoxia, while the high  $\text{N}_2\text{O}$  concentrations ( $> 20$  nM) sporadically occurred at different depths either in spring or autumn.

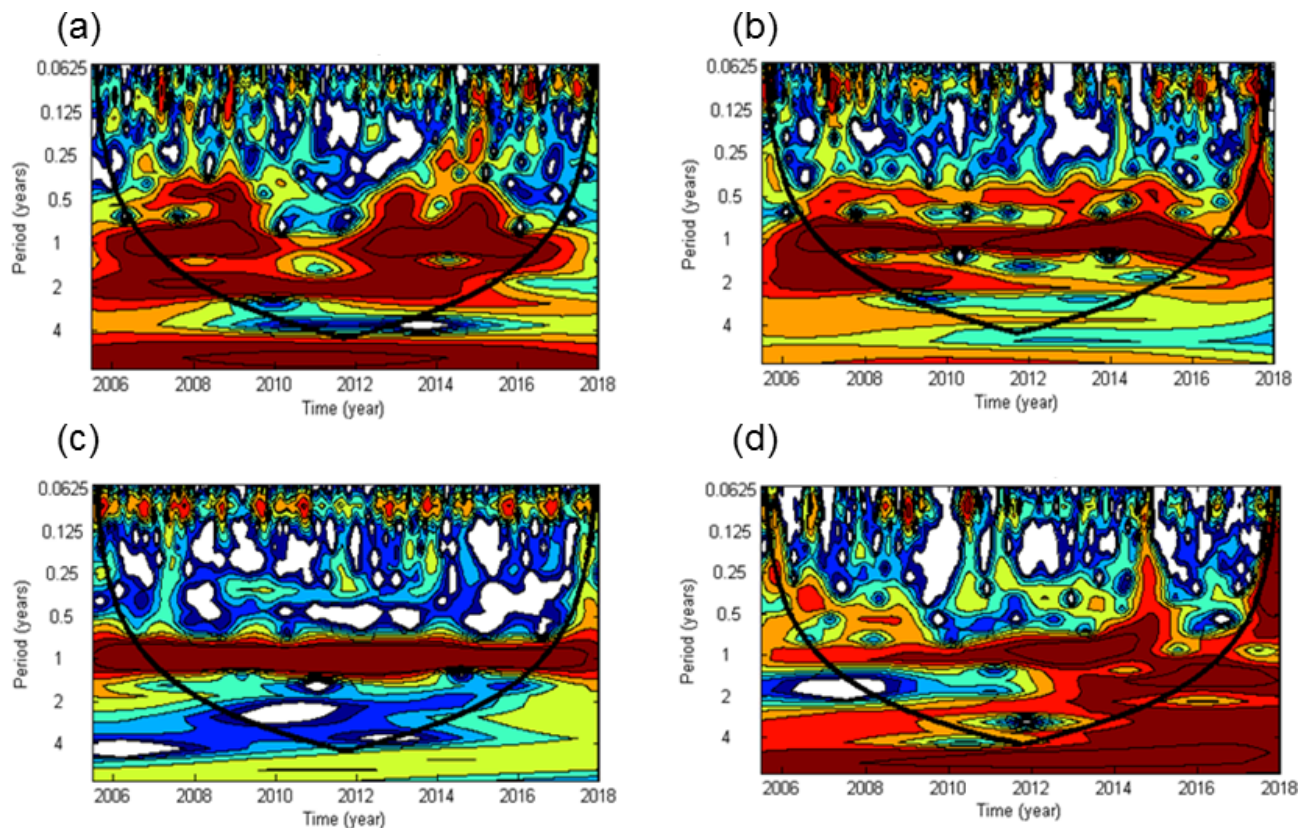
### 3.2 Seasonal cycle

Significant cycles at different frequencies were detected via wavelet analysis at the BE Time Series Station during 2005–2017 (Fig. 3). A half-year  $\text{NO}_2^-$  cycle sporadically occurred in 2007–2009, 2013, and 2015. There is a seasonal  $\text{NO}_2^-$  variability (at the frequency of 1 year) between 2007 and 2016 (times before 2007 and after 2016 were outside the conic line), except during 2010–2012, when high  $\text{NO}_2^-$  concentrations were not observed in winter (Fig. 2). A biennial cycle of  $\text{NO}_2^-$  could be observed as well during 2008–2015. The  $\text{NO}_3^-$  concentrations were dominated by an annual cycle and a minor half-year cycle. The biennial cycle only occurred in 2008 and 2009. A remarkable seasonal variability in dissolved  $\text{O}_2$  prevailed all the time, which is also obvious from the time series data shown in Fig. 2. The annual  $\text{N}_2\text{O}$  cycle became gradually more and more evident until 2014, then declined and reoccurred less intensely in 2016. The periodical cycle was also present at other frequencies, indicated by the broadening of the red area before 2015 in Fig. 2d. For example, a biennial  $\text{N}_2\text{O}$  cycle occurred during 2013–2015.





**Figure 2.** Vertical distributions of dissolved  $O_2$ ,  $NO_2^-$ ,  $NO_3^-$ , and  $N_2O$  from the BE Time Series Station during 2005–2017.



**Figure 3.** Wavelet power spectra of  $NO_2^-$  (a),  $NO_3^-$  (b), dissolved  $O_2$  (c), and  $N_2O$  (d) from the BE Time Series Station. Red areas indicate high power and blue areas indicate low power. The black conic line indicates the significant area where boundary effects can be excluded.

The half-year cycles of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were probably associated with algae blooms which usually occur in each spring and autumn (Figs. S1 and S2 in the Supplement). Since the time between the two blooms differed between years, the cycles were weak and thus not present in every year. Due to the fact that there was no half-year  $\text{O}_2$  cycle at all, nutrients apart from  $\text{O}_2$  might be the “drivers” of the sporadic half-year  $\text{N}_2\text{O}$  cycle in 2008 and 2015 because  $\text{N}_2\text{O}$  production depends on the concentration of the bioavailable nitrogen compounds (Codispoti et al., 2001).

Generally the wavelet analysis indicated a strong annual cycle for  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , dissolved  $\text{O}_2$ , and  $\text{N}_2\text{O}$  at the BE Time Series Station, which enabled us to explore the seasonal pattern with annual mean data. Although extreme values were excluded as a result of averaging, the smoothed results generally reflect the seasonality of these parameters. Here, we focus on the annual cycle.

The annual mean vertical distribution of dissolved  $\text{O}_2$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{N}_2\text{O}$  are shown in Fig. 4. Due to the development of stratification, the mixed layer was shallow in summer and deep in late autumn and winter.  $\text{O}_2$  depletion was observed in bottom waters from late spring until late autumn. The seasonal variations in  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were significantly correlated with each other ( $[\text{NO}_3^-] = 11.59[\text{NO}_2^-] - 0.51$ ,  $R^2 = 0.80$ ,  $n = 72$ ,  $p < 0.0001$ ) and high concentrations were observed for both in winter. Minimum  $\text{N}_2\text{O}$  concentrations were found in the bottom waters during September and October, presumably as a result of consumption during denitrification under anoxic condition (Codispoti et al., 2005). High  $\text{N}_2\text{O}$  concentrations were observed in late spring and late autumn, respectively. In late spring  $\text{N}_2\text{O}$  accumulated in the bottom waters because the stratification prevented mixing of the water column. In late autumn, however,  $\text{N}_2\text{O}$  could be ventilated to the surface and thus emitted to the atmosphere due to the breakdown of the stratification. The high  $\text{N}_2\text{O}$  concentrations could be attributed to enhanced  $\text{N}_2\text{O}$  production via nitrification and/or denitrification within the oxic–anoxic interface (Goreau et al., 1980; Codispoti et al., 1992). Since there is no clear  $\text{O}_2$  concentration threshold,  $\text{N}_2\text{O}$  production from both nitrification and the onset of denitrification overlap at oxic–anoxic interface. To this end, direct  $\text{N}_2\text{O}$  production measurements (i.e. nitrification and denitrification rates) are required to decipher which process dominates the formation of the different  $\text{N}_2\text{O}$  maxima.

High  $\text{N}_2\text{O}$  concentrations prevailed all over the water column in winter and early spring.  $\text{NH}_4^+$  is released from the sediment into bottom waters due to the degradation of organic matter, especially after the autumn algae bloom (Figs. S1 and S2 in the Supplement). The stratification usually completely breaks down at this time of the year and the water column becomes oxygenated. Denitrification is inhibited by the presence of high concentrations of dissolved  $\text{O}_2$  ( $> 20 \mu\text{mol L}^{-1}$ , which is higher than the  $\text{O}_2$  threshold of about  $10 \mu\text{mol L}^{-1}$ ; Tiedje, 1988) and thus nitrification is

presumably responsible for the high  $\text{N}_2\text{O}$  concentrations in winter and early spring.

### 3.3 Trend analysis

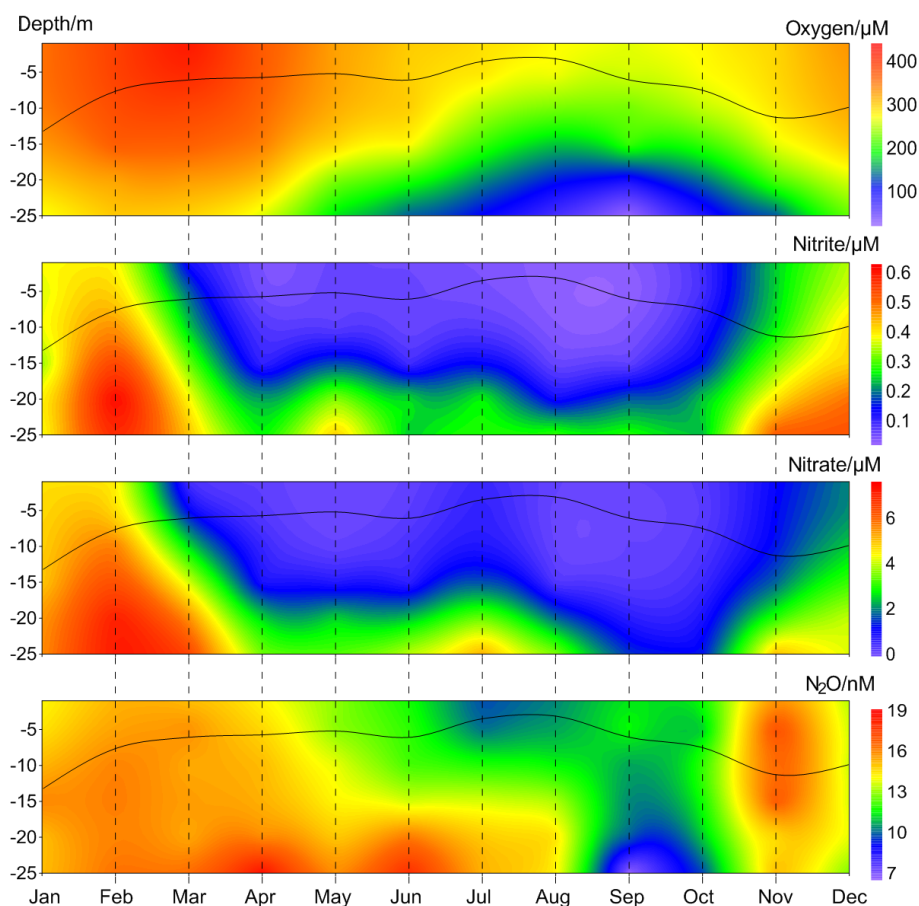
The MKTs were conducted for the surface (1 m) and bottom (25 m)  $\text{N}_2\text{O}$  concentrations and saturations of the individual 12 months, respectively. Significant decreasing trends were detected for the concentrations in the bottom waters for February and August (Table 1a), and for the saturations in the surface for September and in the bottom for August and November (Table 1b). These results indicated that some systematical changes in  $\text{N}_2\text{O}$  took place at BE. For example, the significant decrease in  $\text{N}_2\text{O}$  concentration/saturation in August might be associated with the increasing temperature, which reinforces the stratification and accelerates  $\text{O}_2$  consumption in the bottom waters (Lennartz et al., 2014). As a result, hypoxia/anoxia starts earlier and thus enables the onset of denitrification to consume  $\text{N}_2\text{O}$ . During most of the months, trends in  $\text{N}_2\text{O}$  concentration and saturation were not significant during 2005–2017.

A significant nutrient decline has been observed at the BE Time Series Station since the mid-1980s; however, Lennartz et al. (2014) found that bottom  $\text{O}_2$  concentrations were still decreasing over the past 60 years. The ongoing oxygen decline was attributed to the temperature-enhanced  $\text{O}_2$  consumption in the bottom water (Meier et al., 2018) and a prolongation of the stratification period at the BE Time Series Station (Lennartz et al., 2014). Please note that the trends in nutrients and  $\text{O}_2$  concentrations were detected based on the data collection, which lasted for approximately 30 and 60 years, respectively, while the  $\text{N}_2\text{O}$  observations at BE Time Series Station have lasted for only 12.5 years. Further MKT analysis for nutrients, temperature, and oxygen for months with significant trends in  $\text{N}_2\text{O}$  concentrations did not show any significant results ( $p > 0.05$ ). The significant trends in  $\text{N}_2\text{O}$  concentrations thus do not seem to be directly related to one of these parameters, and we cannot state a reason for the significant trends of  $\text{N}_2\text{O}$  concentration in February and the  $\text{N}_2\text{O}$  saturation in September and November at this point. Presumably, a longer monitoring period for  $\text{N}_2\text{O}$  is required to detect corresponding trends in  $\text{N}_2\text{O}$  and oxygen or nutrients.

### 3.4 Extreme events

#### 3.4.1 Low $\text{N}_2\text{O}$ concentrations during October 2016–April 2017

Besides the low  $\text{N}_2\text{O}$  concentrations occurring in autumn, we observed a band of pronounced low  $\text{N}_2\text{O}$  concentrations which started in October 2016 and lasted until April 2017 (Fig. 5). In this period  $\text{N}_2\text{O}$  concentrations varied between 5.5 and 13.9 nM, with an average of  $8.4 \pm 2.0$  nM. This is approximately 40 % lower than the average  $\text{N}_2\text{O}$  concentration



**Figure 4.** Average vertical distributions of dissolved  $\text{O}_2$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{N}_2\text{O}$  from the BE Time Series Station during 2005–2017. The black line indicates the mixed layer depth, which was calculated based on a potential density anomaly of  $0.15 \text{ kg m}^{-3}$  from the sea surface (1 m).

during the entire measurement period 2005–2017. The average  $\text{N}_2\text{O}$  saturation during 2005–2017 was  $111 \pm 30 \%$ , while from October 2016 to April 2017 the  $\text{N}_2\text{O}$  saturations were as low as 43 %–93 % (average  $62 \pm 10 \%$ ).

Undersaturated  $\text{N}_2\text{O}$  waters have been previously reported from the Baltic Sea: Rönner (1983) observed a  $\text{N}_2\text{O}$  surface saturation of 79 % in the central Baltic Sea and attributed the undersaturation to upwelling of  $\text{N}_2\text{O}$ -depleted waters. Bange et al. (1998) found a minimum  $\text{N}_2\text{O}$  saturation of 91 % in the southern Baltic Sea where the hydrographic conditions were significantly influenced by riverine runoff. Walter et al. (2006) reported a mean  $\text{N}_2\text{O}$  saturation of  $79 \pm 11 \%$  for shallow stations (< 30 m) in the southwestern Baltic Sea in October 2003. The low- $\text{N}_2\text{O}$  event at BE was unusual because the concentrations were much lower than those reported values and it lasted for more than half a year.

Although the observed temperatures and salinities during October 2016–April 2017 were comparable to other years (Fig. S1), it is difficult to evaluate the role of physical mechanism in the low- $\text{N}_2\text{O}$  event because of insufficient data for water mass exchange at the BE Time Series Station.

Here we mainly focused on the chemical or biological processes. Anoxia events with the presence of  $\text{H}_2\text{S}$  were observed in the bottom waters for 3 months in a row during September–November 2016. This is an unusual long period and is unprecedented at the BE Time Series Station. In December 2016 the stratification did not completely break down. Although the water column was generally oxygenated, bottom  $\text{O}_2$  concentrations were the lowest observed during the past 12.5 years. Considering the classical view of  $\text{N}_2\text{O}$  consumption via denitrification under hypoxic and anoxic conditions, we inferred that denitrification accounted for low  $\text{N}_2\text{O}$  concentrations in the bottom layer. However, the question of where the low  $\text{N}_2\text{O}$  concentration water in the upper layers came from still remains.

In September 2016, low  $\text{N}_2\text{O}$  concentrations were only observed in the bottom waters where the anoxia occurred. However, the situation was different in the following months. During October/November 2016,  $\text{N}_2\text{O}$  concentrations were homogeneously distributed in the water column. Although the stratification gradually started to break down in late autumn, the density gradient was still strong enough to keep

**Table 1.** The results of the Mann–Kendall test for the surface and bottom N<sub>2</sub>O concentrations and saturations of the 12 individual months.

(a) MKT results for N <sub>2</sub> O concentrations									
Month	Jan		Feb		Mar		Apr		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.09	0.19	0.11	0.03(–)	0.19	0.63	0.09	0.30	
Month	May		Jun		Jul		Aug		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.63	0.24	0.15	0.95	0.16	0.16	0.20	0.03(–)	
Month	Sep		Oct		Nov		Dec		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.25	0.76	0.36	0.76	0.67	0.16	0.10	0.30	
(b) MKT results for N <sub>2</sub> O saturations									
Month	Jan		Feb		Mar		Apr		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.37	0.24	0.15	0.15	0.19	0.63	0.11	0.19	
Month	May		Jun		Jul		Aug		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.19	1	0.37	0.54	0.10	0.43	0.20	0.02(–)	
Month	Sep		Oct		Nov		Dec		
Depth (m)	1	25	1	25	1	25	1	25	
<i>p</i>	0.04(–)	0.85	0.06	0.43	0.20	0.03(–)	0.16	0.36	

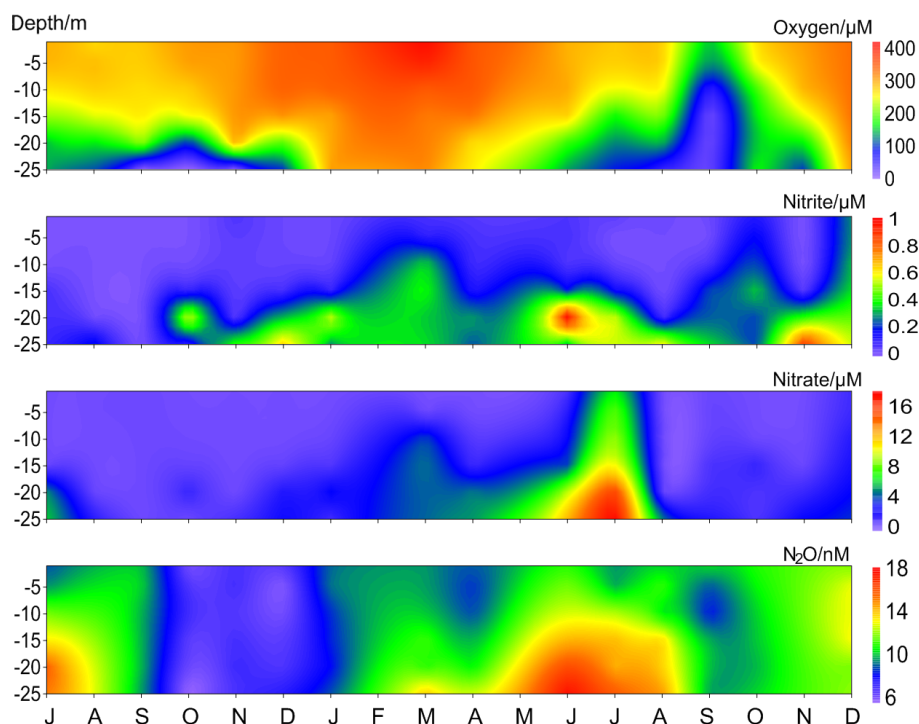
*p* indicates the *p* value of the test, which is the probability, under the null hypothesis, of obtaining a value of the test statistic as extreme or more extreme than the value computed from the sample. (–) indicates a rejection of the null hypothesis at  $\alpha$  significance level and a decreasing trend is detected.

the bottom waters at anoxic conditions and prevented the low-N<sub>2</sub>O-concentration water to reach the surface. Thus we inferred that the unusual low N<sub>2</sub>O concentrations in the upper layers (above 20 m) were probably resulting from advection of adjacent waters. Due to the fact that the upper layers were well-mixed and oxygenated, in situ N<sub>2</sub>O consumption in the water column could be neglected. We suggest, therefore, that the N<sub>2</sub>O-depleted waters were resulting from consumption of N<sub>2</sub>O in bottom waters elsewhere and then they were upwelled and transported to BE. Hence, N<sub>2</sub>O consumption via denitrification might have been, directly or indirectly, responsible for the low N<sub>2</sub>O concentrations during October–November 2016.

In December 2016, the bottom waters were ventilated with O<sub>2</sub>. Although N<sub>2</sub>O consumption by denitrification should have been inhibited by the high concentrations of O<sub>2</sub> (Codispoti et al., 2001), the N<sub>2</sub>O concentrations did not restore to their normal level under suboxic conditions. Since January 2017, the whole water column was well mixed and oxygenated. Usually a significant nutrient supply could be observed starting in November (Fig. 4) as a result of remineralization and vertical mixing, but the average NO<sub>2</sub><sup>–</sup> and NO<sub>3</sub><sup>–</sup> concentrations during November 2016–April 2017 were 0.2

and 1.4 µM, respectively, which was about 50 % and 60 % lower than in other years. Ammonium (NH<sub>4</sub><sup>+</sup>) and chlorophyll *a* concentrations during this period were comparable to those of other years (Fig. S1). Secchi depth, a proxy of water transparency, was 3.8 m in March 2017, which is only slightly lower compared to the monthly average value for March (4.5 ± 1.8 m). There is no exceptional spring algae bloom and thus we infer that assimilative uptake of nutrients by phytoplankton was not responsible for the low nutrient concentrations. The nutrient deficiency might be attributed to enhanced nitrogen removal processes like denitrification or anammox (Voss et al., 2005; Hietanen et al., 2007; Hannig et al., 2007) during the prolonged period of anoxia in autumn 2016. During the low-N<sub>2</sub>O event, we found that N<sub>2</sub>O concentrations were positively correlated with both NO<sub>2</sub><sup>–</sup> ([N<sub>2</sub>O] = 7.02[NO<sub>2</sub><sup>–</sup>] + 7.36,  $R^2 = 0.29$ ,  $n = 24$ ,  $p < 0.01$ ) and NO<sub>3</sub><sup>–</sup> ([N<sub>2</sub>O] = 0.80[NO<sub>3</sub><sup>–</sup>] + 7.36,  $R^2 = 0.51$ ,  $n = 24$ ,  $p < 0.0001$ ). These results indicate that the development and maintenance of the low N<sub>2</sub>O concentration was closely associated with nutrient deficiency. Especially after the breakdown of the stratification, when denitrification was no longer a significant N<sub>2</sub>O sink, nutrients might have become a limiting factor for N<sub>2</sub>O production.





**Figure 5.** Vertical distribution of dissolved  $O_2$ ,  $NO_2^-$ ,  $NO_3^-$ , and  $N_2O$  from the BE Time Series Station during July 2016–December 2017. Please note that the high  $N_2O$  concentrations in November 2017 were removed for better visualization.

In general, the low- $N_2O$ -concentration event during October 2016–April 2017 can be divided into two parts: in the stratified waters during October–November 2016,  $O_2$  played a dominant role and  $N_2O$  was consumed via denitrification under anoxic conditions. In the well-mixed water column during December 2016–April 2017, nutrient deficiency seemed to have constrained  $N_2O$  production via nitrification under suboxic/oxic conditions.

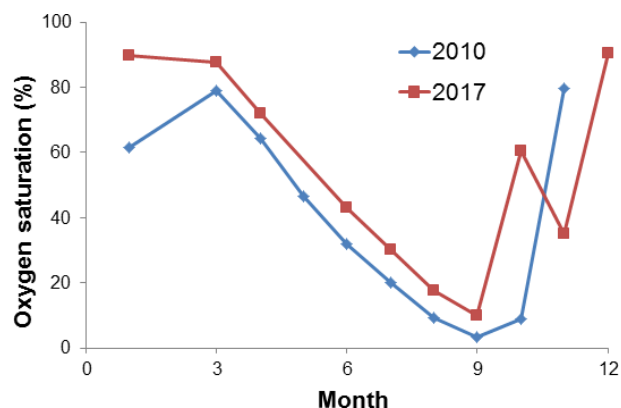
In recent years a novel biological  $N_2O$  consumption pathway, called  $N_2O$  fixation, which transforms  $N_2O$  into particulate organic nitrogen via its assimilation, has been reported (Fariás et al., 2013). This process can take place under extreme environmental conditions even at very low  $N_2O$  concentrations. Cornejo et al. (2015) reported that  $N_2O$  fixation might play a major role in the coastal zone off central Chile where seasonally occurring surface  $N_2O$  undersaturation was observed. The relatively high  $N_2$  fixation rates in the Baltic Sea (Sohm et al., 2011) highlight the potential role of  $N_2O$  fixation (Fariás et al., 2013). However, we cannot quantify the role of biological  $N_2O$  fixation for the  $N_2O$  depletion in the Baltic Sea due to the absence of  $N_2O$  assimilation measurements.

### 3.4.2 High $N_2O$ concentrations in November 2017

High  $N_2O$  concentrations were observed at the BE Time Series Station in November 2017. The average value reached  $35.4 \pm 1.5$  nM, which was the highest concentration measured

during the entire sampling period from 2005 to 2017. Dissolved  $N_2O$  was homogeneously distributed in the water column, but this event did not last long. In December, dissolved  $N_2O$  returned to normal levels and the average concentration in the water column was comparable to that of other years. Average  $N_2O$  saturation in November 2017 was  $322 \pm 10$  %, which was also the highest for the past 12.5 years. This value was much higher than the maximum surface  $N_2O$  saturation reported by Rönner (1983) in the central Baltic Sea but was comparable to the results observed in the southern Baltic Sea (312 %; Bange et al., 1998). Bange et al. (1998) linked the enhanced  $N_2O$  concentrations to riverine runoff because those samples were collected in an estuarine area; however, the riverine influence around the BE Time Series Station is negligible. As a result, the impact of fresh water input can be excluded.

Dissolved  $O_2$  seemed to play a dominant role in the high  $N_2O$  concentrations. Enhanced  $N_2O$  production usually occurred at the oxic–anoxic interface, which was closely linked to the development of water column stratification. In general the breakdown of the stratification is faster than its establishment at the BE Time Series Station. As a result, it took about half a year for bottom  $O_2$  saturation to gradually decrease from  $\sim 80$  % to almost 0 % (i.e. anoxia) but only 2 months to restore normal saturation level in 2010 (Fig. 6). In late autumn, surface water penetrated into the deep layers via vertical mixing and eroded the oxic–anoxic interface. The entire



**Figure 6.** Variations of bottom O<sub>2</sub> saturation in 2010 (blue) and 2017 (red).

water column quickly became oxygenated and the enhanced N<sub>2</sub>O production was stopped.

Hypoxia or anoxia at BE is usually observed in the bottom waters in autumn, but in September 2017 hypoxic water (O<sub>2</sub> saturation < 20 %, which was close to the criterion for hypoxia; see Naqvi et al., 2010) was found in the subsurface layer (10 m) as well. Surface O<sub>2</sub> saturation was only ~ 50 %, which was the lowest during the sampling period 2005–2017. The density gradient of the water column in September 2017 was much lower than in other years. These results indicate the occurrence of an upwelling event at BE Time Series Station in autumn 2017, which might be a result of the saline water inflow from the North Sea considering the change of salinity in the water column (Fig. S1). Strong vertical mixing has interrupted the hypoxia/anoxia and bottom O<sub>2</sub> saturation reached ~ 60 % in October 2017. The presence of O<sub>2</sub> prevented N<sub>2</sub>O consumption via denitrification; as a result, we did not observe a significant N<sub>2</sub>O decline during that period (Fig. 5).

Considering the fact that a significant autumn algae bloom was observed in autumn 2017 (as indicated by high chlorophyll *a* concentrations, see Fig. S1), severe O<sub>2</sub> depletion in the bottom water could be expected. Although the bottom O<sub>2</sub> saturation was only slightly lower in November than in October, we speculate that even lower O<sub>2</sub> saturation (but not anoxia) might have occurred between October and November. The “W-shaped” O<sub>2</sub> saturation curve (see Fig. 6) suggests that the stratification did not completely break down in October and that there might have been a reestablishment of the oxic–anoxic interface providing favourable conditions for enhanced N<sub>2</sub>O production. Due to the degradation of organic nitrogen, NH<sub>4</sub><sup>+</sup> is released from the sediment into bottom waters (Dale et al., 2011), especially in autumn when O<sub>2</sub> is low (Fig. S2). NH<sub>4</sub><sup>+</sup> concentrations in November 2017 were lower than in other years (Fig. S1), and NO<sub>2</sub><sup>−</sup> concentrations were higher (Fig. 5), indicating that nitrification occurred in bottom waters. To this end, we suggest that the reestablishment of the oxic–anoxic interface promoted ammonium oxidation

(the first step of nitrification). In this case, N<sub>2</sub>O could have temporarily accumulated because its consumption via denitrification was blocked. Meanwhile, the relatively low density gradient (i.e. low stratification) allowed upward mixing of the excess N<sub>2</sub>O to the surface. However, we inferred that this phenomenon would only last for a few days due to the rapid breakdown of stratification at the BE Time Series Station.

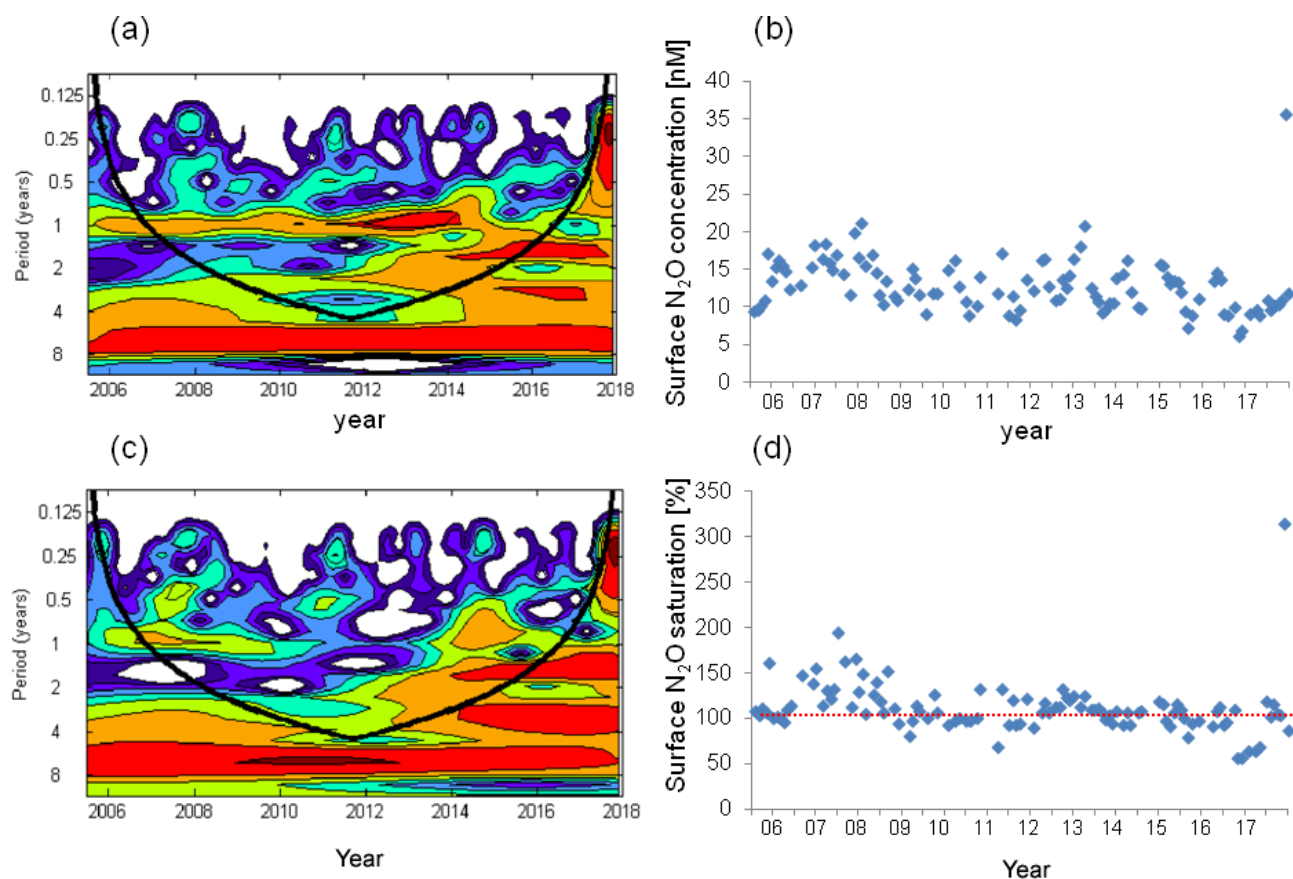
Due to the development of the pronounced stratification, the oxic–anoxic interface prevailed in summer/early autumn as well, but we did not observe N<sub>2</sub>O accumulation during these months. One of the potential explanations is that enhanced N<sub>2</sub>O production only took place within particular depths where strong O<sub>2</sub> gradient existed, but our vertical sampling resolution was too low to capture this event. Also enhanced N<sub>2</sub>O production might be covered by the weak mixing which brought low-N<sub>2</sub>O water from the bottom to the surface.

The upwelling event played different roles in autumn 2016 and 2017. First, upwelling took place somewhere else but at BE because of the strong density and O<sub>2</sub> gradient in the water column during autumn 2016. Second, bottom water remained anoxic in autumn 2016, while the compensated water for upwelling in 2017 penetrated through stratification and brought O<sub>2</sub> into bottom water (Fig. 6), which caused enhanced N<sub>2</sub>O production. Similarly, autumn upwelling was detected in 2011 and 2012 when we found relatively low O<sub>2</sub> concentrations in subsurface layers (10 m) (Fig. 2), but we did not observe an increase in bottom O<sub>2</sub> concentrations and N<sub>2</sub>O concentrations remained low during that time. These upwelling events seem to be driven by saline water inflow considering the prominent increase in salinity, but the mechanism that dominates O<sub>2</sub> input into bottom water before the stratification break down remains unclear.

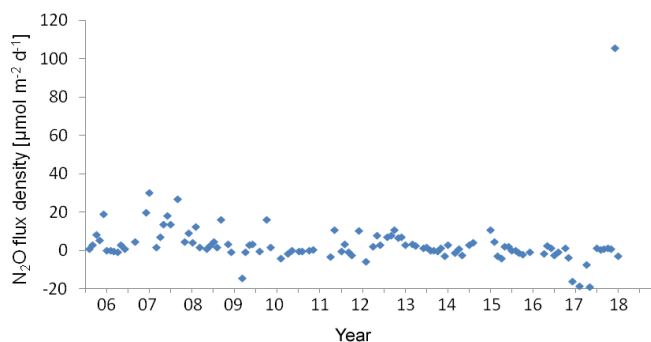
### 3.5 Flux density

During 2005–2017, surface N<sub>2</sub>O saturations at the BE Time Series Station varied from 56 % to 314 % (69 %–194 % excluding the extreme values discussed in Sect. 3.4), with an average of  $111 \pm 30$  % ( $111 \pm 20$  % without the extreme values). Generally the water column at BE was slightly oversaturated with N<sub>2</sub>O. Our results are in good agreement with the estimated mean surface N<sub>2</sub>O saturation for the European shelf (113 %; Bange, 2006).

We found a weak seasonal cycle for surface N<sub>2</sub>O concentrations, with high N<sub>2</sub>O concentrations occurring in winter and early spring and low concentrations occurring in summer/autumn, but no such cycle for N<sub>2</sub>O saturation (Figs. 4, 7). The seasonality in concentration but not in saturation could be largely attributed to the effect of temperature on N<sub>2</sub>O solubility: in summer when surface N<sub>2</sub>O concentrations are low, N<sub>2</sub>O saturations are increased by the relative high temperature and vice versa in winter. Although salinity also affects N<sub>2</sub>O solubility, its contribution is negligible compared to temperature. Temperature alleviated the fluctua-



**Figure 7.** Wavelet analysis and the variation in surface  $\text{N}_2\text{O}$  concentrations (a, b) and surface  $\text{N}_2\text{O}$  saturations (c, d). The dashed red line in (d) indicates the saturation of 100 %.



**Figure 8.** Variation of  $\text{N}_2\text{O}$  flux density at the BE Time Series Station during 2005–2017. Negative values indicated  $\text{N}_2\text{O}$  influx from the atmosphere and positive values indicated  $\text{N}_2\text{O}$  efflux to the atmosphere.

tion of surface  $\text{N}_2\text{O}$  saturation and thus affected the sea-to-air  $\text{N}_2\text{O}$  fluxes. We conclude that temperature plays a modulating role for  $\text{N}_2\text{O}$  emissions.

The wind speed ( $u_{10}$ ) at the BE Time Series Station ranged from  $1.1$  to  $14.0 \text{ m s}^{-1}$ , with an average of  $7.0 \pm 2.7 \text{ m s}^{-1}$ .  $\text{N}_2\text{O}$  flux densities varied from  $-19.0$  to  $105.7 \mu\text{mol m}^{-2} \text{ d}^{-1}$

( $-14.1$  to  $30.3 \mu\text{mol m}^{-2} \text{ d}^{-1}$  without the extreme values), with an average of  $3.5 \pm 12.4 \mu\text{mol m}^{-2} \text{ d}^{-1}$  ( $3.3 \pm 6.5 \mu\text{mol m}^{-2} \text{ d}^{-1}$  without the extreme values). However, the true emissions might have been underestimated because our monthly sampling resolution is insufficient to capture short-term  $\text{N}_2\text{O}$  accumulation events due to the fast breakdown of stratification in autumn. The uncertainty introduced in the flux density computation was estimated to be 20 % (Wanninkhof, 2014). The flux densities at the BE Time Series Station are comparable to those reported by Bange et al. (1998,  $0.4$  to  $7.1 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) from the coastal waters of the southern Baltic Sea but are slightly lower than the average  $\text{N}_2\text{O}$  flux density reported by Rönner (1983,  $8.9 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) from the central Baltic Sea. Please note that the results of Rönner (1983) were obtained only from the summer season and therefore are probably biased because of missing seasonality.

In December 2014, a strong saline water inflow from the North Sea was observed, which was the third strongest ever recorded (Mohrholz et al., 2015). Although the salinity in December 2014 was comparable to other years, a remarkable increase in salinity was observed in the following several months. However, we did not detect a significant  $\text{N}_2\text{O}$

anomaly or enhanced emission during that time. Similarly, Walter et al. (2006) investigated the impact of the North Sea water inflow on  $\text{N}_2\text{O}$  production in the southern and central Baltic Sea in 2003. The oxygenated water ventilated the deep Baltic Sea and shifted anoxic to oxic condition which led to enhanced  $\text{N}_2\text{O}$  production, but the accumulated  $\text{N}_2\text{O}$  was unlikely to reach the surface due to the presence of a permanent halocline (Walter et al., 2006).

Although we observed an extremely high  $\text{N}_2\text{O}$  flux density in November 2017, the low- $\text{N}_2\text{O}$ -concentration ( $< 10 \text{ nM}$ ) events have become more and more frequent during the past 12.5 years (Fig. 2). This phenomenon seldom occurred before 2011, but remarkable low  $\text{N}_2\text{O}$  concentrations can be seen in 2011 and 2013, and to a lesser extent in 2012 and 2014. Similar events lasted for several months in 2015 and for even more than half a year during 2016–2017. The most striking feature was that the low- $\text{N}_2\text{O}$ -concentration water was not only detected in bottom waters but also at surface which would significantly impact the air–sea  $\text{N}_2\text{O}$  flux densities. Although the MKT result did not give a significant trend for the  $\text{N}_2\text{O}$  flux densities, the data presented in Fig. 8 suggest a potential decline of  $\text{N}_2\text{O}$  flux densities from the coastal Baltic Sea, challenging the conventional view that  $\text{N}_2\text{O}$  emissions from coastal waters would most probably increase in the future, which was based on the hypothesis of increasing nutrient loads into coastal waters. Due to an effective reduction of nutrient inputs, the severe eutrophication condition in the Baltic Sea has been alleviated (HELCOM, 2018b), but ongoing deoxygenation points to the fact that it will take a longer time for coastal ecosystems to feedback to reduced nutrient inputs because other environmental changes such as warming may override decreasing eutrophication (Lennartz et al., 2014).

#### 4 Conclusions

The seasonal and inter-annual  $\text{N}_2\text{O}$  variations at the BE Time Series Station from July 2005 to December 2017 were driven by the prevailing  $\text{O}_2$  regime and nutrient availability. We found a pronounced seasonal cycle with low  $\text{N}_2\text{O}$  concentrations (undersaturations) occurring in hypoxic or anoxic bottom waters in autumn and enhanced concentrations (supersaturations) all over the water column in winter and early spring. Significant decreasing trends for  $\text{N}_2\text{O}$  concentrations were found for few months, while most of the year no significant trend was detectable in the period of 2005–2017. During 2005–2017, no significant trends were present for  $\text{O}_2$  or nutrients either, but these parameters all show significant decreasing trends on longer timescales ( $\sim 60$  years) at BE. Our results show the strong coupling of  $\text{N}_2\text{O}$  with  $\text{O}_2$  and nutrient concentrations, and suggest similar changes on comparable timescales. Further monitoring of  $\text{N}_2\text{O}$  at BE Time Series Station is thus important to detect changes. Further studies on  $\text{N}_2\text{O}$  production and consumption by nitrification

and denitrification and analysis of the characteristic  $\text{N}_2\text{O}$  isotope signature might be very helpful to decipher the potential roles of  $\text{O}_2$  and nutrients for  $\text{N}_2\text{O}$  cycling.

Temperature plays a modulating role for the  $\text{N}_2\text{O}$  emission at the BE Time Series Station. Although the hydrographic condition at BE is generally dominated by the inflow of saline North Sea water, this did not affect  $\text{N}_2\text{O}$  production and its emissions to the atmosphere. It seems that events with extremely low  $\text{N}_2\text{O}$  concentrations and thus reduced  $\text{N}_2\text{O}$  emissions became more frequent in recent years. Our results provide a new perspective on potential future patterns of  $\text{N}_2\text{O}$  distribution and emissions in coastal areas. Continuous measurement at the BE Time Series Station with a focus on late autumn would be of great importance for monitoring and understanding the future changes in  $\text{N}_2\text{O}$  concentrations and emissions in the southwestern Baltic Sea.

**Data availability.** Data are available from the Boknis Eck Database: <https://www.bokniseck.de> (Bange and Malien, 2019) and MEMENTO (the MarinE MethanE and NiTrous Oxide database, <https://memento.geomar.de>, Kock and Bange, 2015, last accessed: 23 October 2019).

**Supplement.** The supplement related to this article is available online at: <https://doi.org/10.5194/bg-16-4097-2019-supplement>.

**Author contributions.** XM, STL, and HWB designed the study and participated in the fieldwork.  $\text{N}_2\text{O}$  measurements and data processing were done by XM and STL. XM wrote the article with contributions from STL and HWB.

**Competing interests.** The authors declare that they have no conflict of interest.

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